

GB225494

Publication Title:

Improvements in or relating to methods of operating and lining electrolytic cells for electrolytic refining

Abstract:

Abstract of GB 225494

(A) 225,494. Aluminum Co. of America, (Assignees of Tilson, D. H.). Nov. 30, 1923, [Convention date]. Aluminium, obtaining. - A process of putting an electric cell in condition for refining a metal comprises establishing in the cell in suitable order upper and lower metallic layers 36, 34 of different densities and an intermediate layer of electrolyte 33 of intermediate density, and before the layer 36 is established freezing a crust from the electrolyte on to the sides of the cell to serve as part of a side lining 32 and after the layer 36 is established completing the formation of the lining. The cell comprises upper and lower steel shells 11, 10 insulated from one another and provided with water jackets 14, 13. The shell 10 has a carbon bottom 24 provided with a conductor 26 and resting on a layer of bauxite 23.; When refining aluminium the electrodes 29 are lowered into contact with the carbon bottom and current is passed to raise the latter to red heat. The cell is then charged with an electrolyte consisting of sodium and aluminium fluorides with the addition of barium and/or strontium fluorides and current is passed therethrough. Sufficient anode alloy, consisting of aluminium, copper, and silicon is then added in a molten or solid form to raise the level of the electrolyte above the joint between the shells. The cooling action of the jackets causes the formation of a crust 32 on the sides of the cell and covering the joint. The cathode metal consisting of part aluminum is now added by pouring it slowly on the asbestos board inclined at an acute angle to the cell.; The electrolyte creeps up the side of the cell by capillary attraction and solidifies thereon to complete the formation of the lining on the part surrounding the cathode.

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PATENT SPECIFICATION



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COMPLETE SPECIFICATION.

Improvements in or relating to Methods of Operating and Lining Electrolytic Cells for Electrolytic Refining.

We, ALUMINUM COMPANY OF AMERICA, a corporation of State of Pennsylvania, United States of America, of Oliver Building, Pittsburgh, Pennsylvania, 5 United States of America, Assignees of DONALD HEATH TILSON, a citizen of the United States of America, of Badin Club, Badin, North Carolina, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to starting, or 15 putting into condition for operation, electrolytic cells for the refining of metal, particularly cells of the type in which the impure metal or alloy, the electrolyte or bath, and the refined metal 20 deposited at the cathode, are in the molten state. The chief object of the invention is to provide for the purpose a method which can be performed in a short period of time, even under unfavor- 25 able conditions, with a minimum of labour, without excessive consumption of electric power, and without injury to the apparatus.

According to this invention, the process 30 of putting an electrolytic cell in condition for electrolytic refining of metal comprises establishing in the cell in suitable order upper and lower molten metallic layers of different densities and 35 an intermediate layer of fused electrolyte of intermediate density, and before the upper metallic layer is established freezing from the electrolyte on the side of the cell a crust adapted to serve as part of 40 a side-lining; and after the said upper metallic layer is established, completing the formation of the side lining.

A cell of the type referred to, as designed particularly for the electrolytic

separation of aluminium in metallic form 45 from an alloy thereof, is illustrated in the accompanying drawings, in which

Fig. 1 is a cross section showing the cell in use, with the molten anode metal or alloy in the bottom of the cell, the 50 fused electrolyte floating on the anode alloy, and the molten cathode metal floating on the electrolyte.

Figs. 2, 3, 4 and 5 are diagrammatic cross sections illustrating various stages 55 in our present process.

The cell illustrated comprises a lower steel shell 10 of cylindrical form and an upper steel shell 11, the two constituting 60 the lower and upper sections of the complete shell. The shell sections are secured together in any convenient manner, and are electrically separated or insulated from each other, as indicated 65 by the insulating ring or gasket 12. They may be also provided with suitable cooling means, in the present instance water jackets 13, 14, in the neighborhood of the joint between the two sections. Cooling water is supplied 70 to the lower jacket through a pipe 15 and inlet nipple 16 and flows in both directions to an outlet pipe 17. Thence it passes through pipe 18 and inlet nipple 75 19 to the upper water jacket, in which it flows in both directions to the outlet nipple 20 and thence through pipe 21 to the waste pipe 22. To prevent electrical grounding, rubber hose may be used for the pipe 15 and 21 and rubber hose may 80 be used for the pipe 18 to prevent material flow of current from the one cell section to the other. In the bottom is a layer of heat-insulating material 23, as for example powdered bauxite, and on 85 this is a bottom lining 24 of conducting material, preferably carbon. Electrical connection, between the lower shell and

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the carbon lining therein, and the external circuit or source of current, not shown, may be made by means of a terminal or busbar 26 associated with the carbon lining in any convenient and suitable manner. The carbon bottom, which constitutes what may for convenience be termed the lower electrode of the cell, is formed with a cavity or depression in its top, as indicated, and with a tapping hole 27 which may be closed by a plug 28 of suitable refractory material. The upper means for connecting the cell contents with the external circuit or source of current comprises a suitable number of short thick cylinders 29 in the upper ends of which the copper or other metal rods 30 are secured. These rods are clamped or otherwise secured by suitable means, not shown to the negative terminal or busbar 31. The cylinders 29 are preferably made of graphite.

On the sides of the cell is a thermally and electrically insulating lining 32 in close union with the carbon bottom 24 and extending over the joint between the shell sections to a plane well up in the upper section. Our present process includes the depositing of the side-lining or crust 32 on the sides of the cell, above but in close contact with the marginal portions of the carbon bottom lining. It may, therefore, be assumed that when the cell is ready for the present process it is substantially like that illustrated in Fig. 1, except for the presence of the side crust or lining and the molten contents hereinafter described.

The first step of our process as carried out in the preferred way is to heat the carbon bottom lining. This is efficiently accomplished by lowering the graphite connectors or electrodes 29 into contact with the carbon bottom, as in Fig. 2 for example, and then connecting the cell terminals to the appropriate terminals of a suitable source (not shown) of direct current. Upon closing the circuit the flow of current through the high resistance encountered at the points of contact between the graphite connectors and the carbon bottom causes rapid and great evolution of heat at such points. When the carbon bottom lining has been well heated up, with considerable portions of it showing a dull red, we cut the cell out of the circuit and pour into the cell a suitable quantity of electrolyte or bath, which has in the meantime been melted in any suitable furnace, not shown. The nature of the electrolyte depends, of course, upon the use to which the cell is to be put. If aluminium is to be refined the best electrolyte that we know of for the purpose is composed of

a mixture of sodium and aluminum fluorides with the addition of barium or strontium fluoride or both. A fused bath compounded of the salts mentioned is of greater density than molten aluminium and is capable of dissolving a considerable quantity of alumina. In some cases it is desirable in the crust-forming stage of our process to have a substantial amount of alumina in the bath, say enough to saturate the same. It is to be understood, however, that the presence of alumina is not essential.

The cell is now connected to the circuit again and the connectors or electrodes 29 are raised, far enough to leave only their lower ends dipping into the molten bath, say to the extent of an inch or two. This stage is represented in Fig. 3, in which the molten bath is indicated at 33. Electrolysis now takes place, but has apparently no useful result except to maintain or increase the temperature of the molten bath. The electrical heating is, however, very important during the rest of the starting process, as it enables us to maintain the cell contents in the molten state at the working temperature at all times, and makes us independent not only of possible delays in obtaining anode alloy or cathode metal but also of variations in their preliminary temperatures. If adequate supplies of superheated molten bath, anode alloy and cathode aluminium are available, and the labor and mechanical conditions are such that the proper amounts of the materials named can be tapped into crucibles and brought to the cell at such a rate that the three substances can be deposited in rapid succession it is possible to start the cell without passing current through it (except, in some cases, for the preliminary heating of the carbon bottom) until all three layers are in place. However, if there is any delay, or if the anode alloy or the cathode metal becomes cooled below the freezing point of the electrolyte, portions of the latter may solidify at its upper or lower surface, as the case may be. Then when the current is applied, its concentration at the still fused areas of the electrolyte may be so great as to cause a swirling or boiling action (due to the magnetic fields present) which may be violent enough to cause the two metal layers to unite and thus require the operation to be stopped and the cell dug out and re-started.

Having established in the cell a layer of electrolyte carrying current as above described, we next introduce a suitable quantity of previously melted anode metal or alloy. For aluminium refining

the anode metal must be heavier than the bath, so that it will sink through the bath to the bottom of the cell. Preferably the aluminium-containing anode metal is an alloy of aluminium, copper and silicon, low in iron and titanium. The anode alloy is supplied preferably through a trough (not shown) which delivers it to the center of the cell, pouring rather slowly so as to raise the bath layer gradually and avoid mixing the alloy therewith. Enough anode alloy is introduced to bring the upper surface of the bath layer well above the insulating joint between the two shell sections 10, 11 (say an inch or so above) as in Fig. 4, in which the anode alloy is indicated at 34; but not enough to bring the alloy itself into contact with the shell. As the bath mixture rises in contact with the shell the cooling effect of the water jackets 13, 14 causes a crust to freeze on the shell walls over the joint between the two sections. This crust, indicated at 32a, Fig. 4, is substantially free from metal and has high insulating properties, electrically as well as thermally, and may attain a thickness of two inches or more. If the bath is saturated with or contains a substantial amount of alumina a considerable portion of the latter freezes out in crystalline corundum-like form, making the side crust more refractory and giving it better insulating properties, and at the same time diminishing the alumina content of the fluid electrolyte well below the saturation point.

The anode alloy is preferably supplied to the cell in molten form, but it may be in solid form. In the latter case, however, it must be melted by electrical heat, which entails considerably longer time for starting the cell. This increase of time is disadvantageous not only because of the delay involved, but also because during the melting period the graphite connectors are carrying all the current as cathodes in direct contact with the bath, thus subjecting them to attack and consequent injury thereby. As the anode alloy is being deposited in the cell, or immediately after, the graphite connectors are raised, leaving them dipping into the floating electrolyte to the extent of only an inch or two.

A layer of molten aluminium, preferably the purest available, is now deposited on the layer of fused electrolyte. By preference this is done by pouring the metal slowly on an asbestos board, as 35, Fig. 5, extending over the edge of the cell, so that as the metal runs into the cell it will meet the electrolyte at an acute angle and hence will not be carried down into contact with

the impure anode metal or alloy. During this addition of the cathode metal the graphite electrodes are again raised so that at the end of the operation they dip only into the molten cathode metal, represented by the layer 36, Fig. 5, and become mere connectors between the cathode and the negative busbar 31, rather than cathodes in contact with the bath. The asbestos board or other guide used in running the cathode metal into the cell is removed as soon as possible.

As the cathode metal is added, molten bath begins to creep up by capillary action between the steel shell and the adjoining cathode metal, and as a result of the cooling due to the water jackets freezes there to form the side-lining or crust 32, Fig. 1, above the lower portion shown at 32a in Figs. 3, 4 and 5. The formation of the crust to the desired thickness can be greatly accelerated by depositing solid electrolyte in powdered form (with or without additional alumina) on the inwardly and downwardly sloping sides of the upper shell section 10, so that it works down between the same and the molten aluminium, where molten electrolyte coming up from below by capillary attraction causes it to frit together, thus forming in a short time a sufficiently thick crust having the desired insulating properties.

The cell is now in a condition such as is illustrated in Fig. 1, with the refining process in operation. By the use of our method we have been able to bring the starting period, during which the several molten layers are established in the cell and the side-lining formed, down to less than 20 minutes for a cell large enough for approximately 1200 pounds of anode alloy, 1500 pounds of electrolyte, and 600 pounds of cathode aluminium, but the time usually runs over a half-hour on account of delays so apt to occur in handling large quantities of different molten materials at temperatures in the neighborhood of 1000° C.

The preliminary heating of the carbon bottom of the cell is advantageous in preventing cracking of the lining and spattering of the fluid bath as it is poured in, both of which may occur if the bath is poured upon the cold lining. The spattering is very apt to be dangerous if for any reason a little moisture has accumulated at any point in the lining. If electrolyte in the molten state is not available the desired layer may be formed by melting the powdered mixture in the cell bottom by the heat evolved at the points of contact with the graphite electrodes, but the

time, labor, and graphite consumption are then much greater.

While we have described our process in conjunction with a method of refining aluminium it can be used to advantage with the electrolytic refining of other metals with a suitable electrolyte.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. The process of putting an electrolytic cell in condition for electrolytic refining of metal, comprising establishing in the cell in suitable order upper and lower molten metallic layers of different densities and an intermediate layer of fused electrolyte of intermediate density, and before the upper metallic layer is established freezing from the electrolyte on the sides of the cell a crust adapted to serve as part of a side-lining; and after the said upper metallic layer is established, completing the formation of the side lining.

2. The process of putting an electrolytic cell in condition for electrolytic refining of metal, comprising establishing in the bottom of the cell a body of molten electrolyte adequate in amount to form a layer of suitable thickness for the subsequent refining operation; establishing in the cell a body of molten metal denser than the electrolyte and in amount adapted to raise the electrolyte to a position suitable for the subsequent refining operation; freezing on the sides of the cell from the electrolyte layer in contact therewith, a crust adapted to form part of a side-lining; establishing on the electrolyte layer a layer of molten metal less dense than the electrolyte and of a thickness suitable for the subsequent refining operation; and after the last-mentioned metallic layer is established completing the formation of the side-lining.

3. The process of putting an electrolytic cell in condition for electrolytic refining of metal, as claimed in Claim 1,

in which while the said molten bodies are being established the mobility of the cell contents is maintained by passing current therethrough.

4. A process for putting an electrolytic cell in condition for electrolytic refining as hereinbefore claimed, in which the refractory bottom of the cell is heated prior to the establishing of the molten layers of electrolyte and metal therein.

5. A process of putting an electrolytic cell in condition for electrolytic refining as hereinbefore claimed in which a body of molten electrolyte is established in the cell after which metal needed in the electrolytic refining and having greater density than the electrolyte is supplied to the cell in molten form and by pouring it slowly so as to position the electrolyte and the metal at heights suitable for the electrolytic refining without mixing the two.

6. A process of putting an electrolytic cell in condition for electrolytic refining as hereinbefore claimed, in which the body of molten metal less dense than the electrolyte is poured thereon slowly and in a stream inclined to the surface thereof.

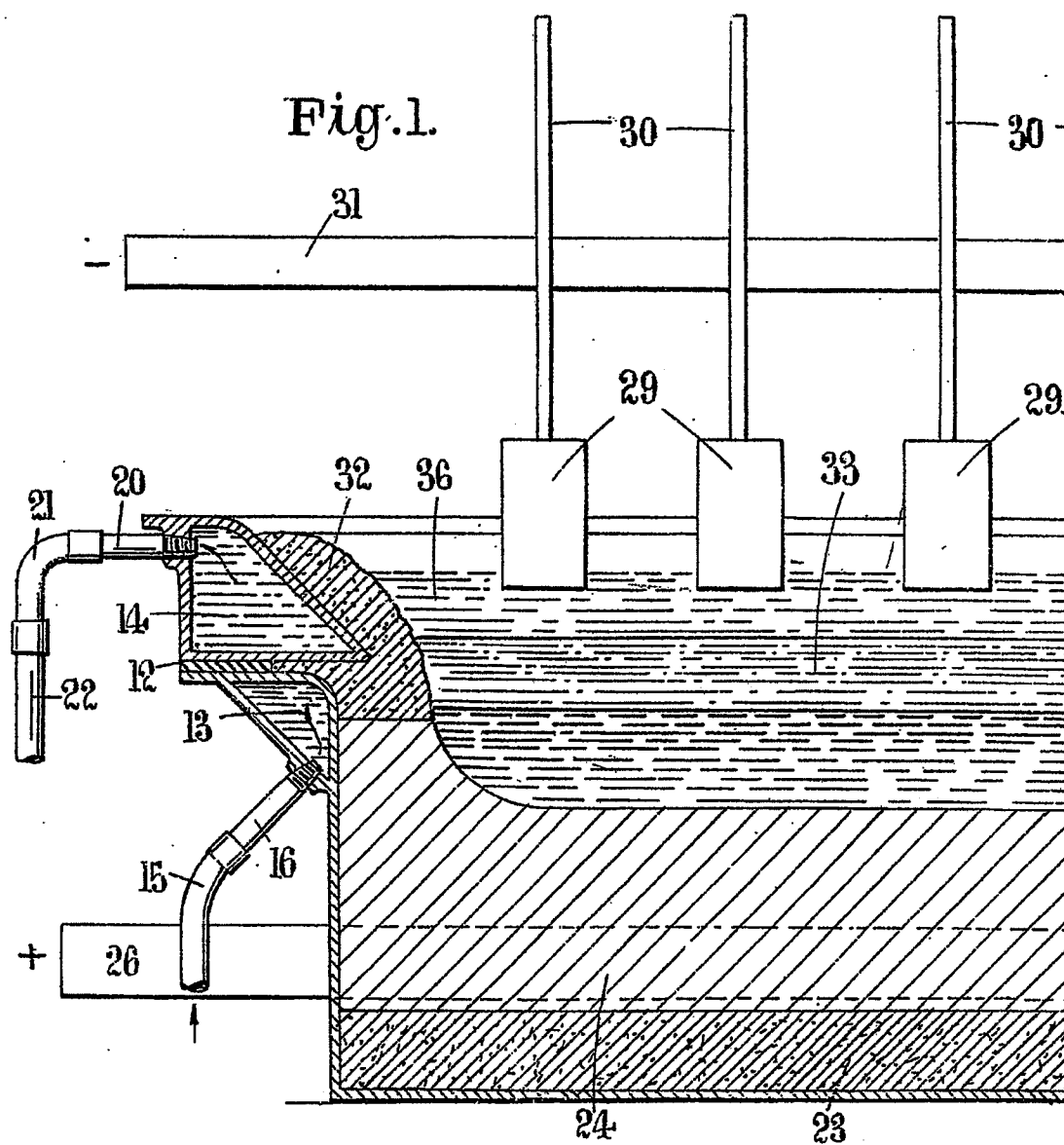
7. A process according to Claim 4, in which the side-lining is formed between the cell wall and the electrolyte and upper metallic layer by freezing same from the electrolyte layer with the addition of electrolyte material in solid form.

8. A process for putting an electrolytic cell in condition for electrolytic refining substantially as hereinbefore described with reference to the accompanying drawings for the purpose specified.

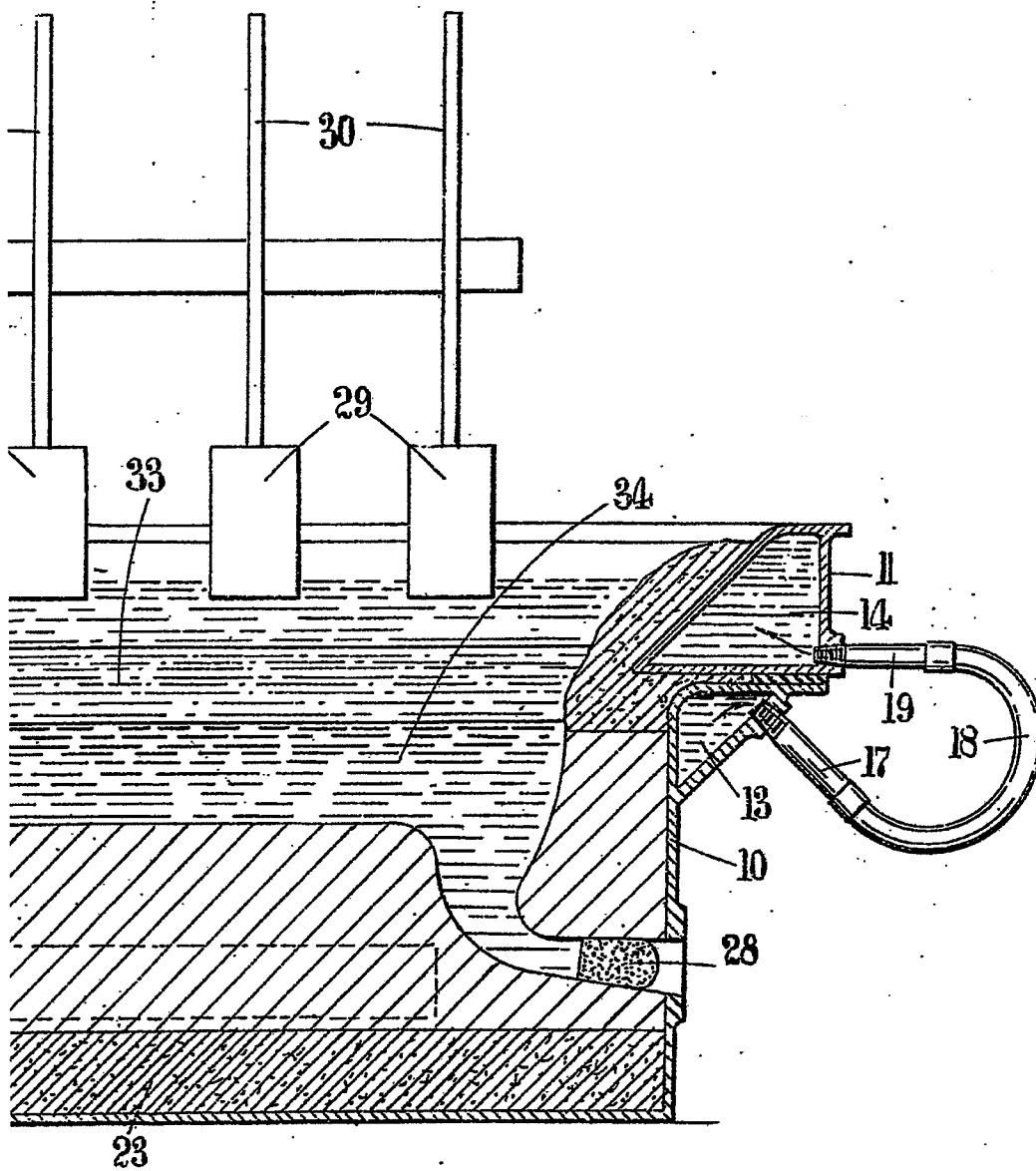
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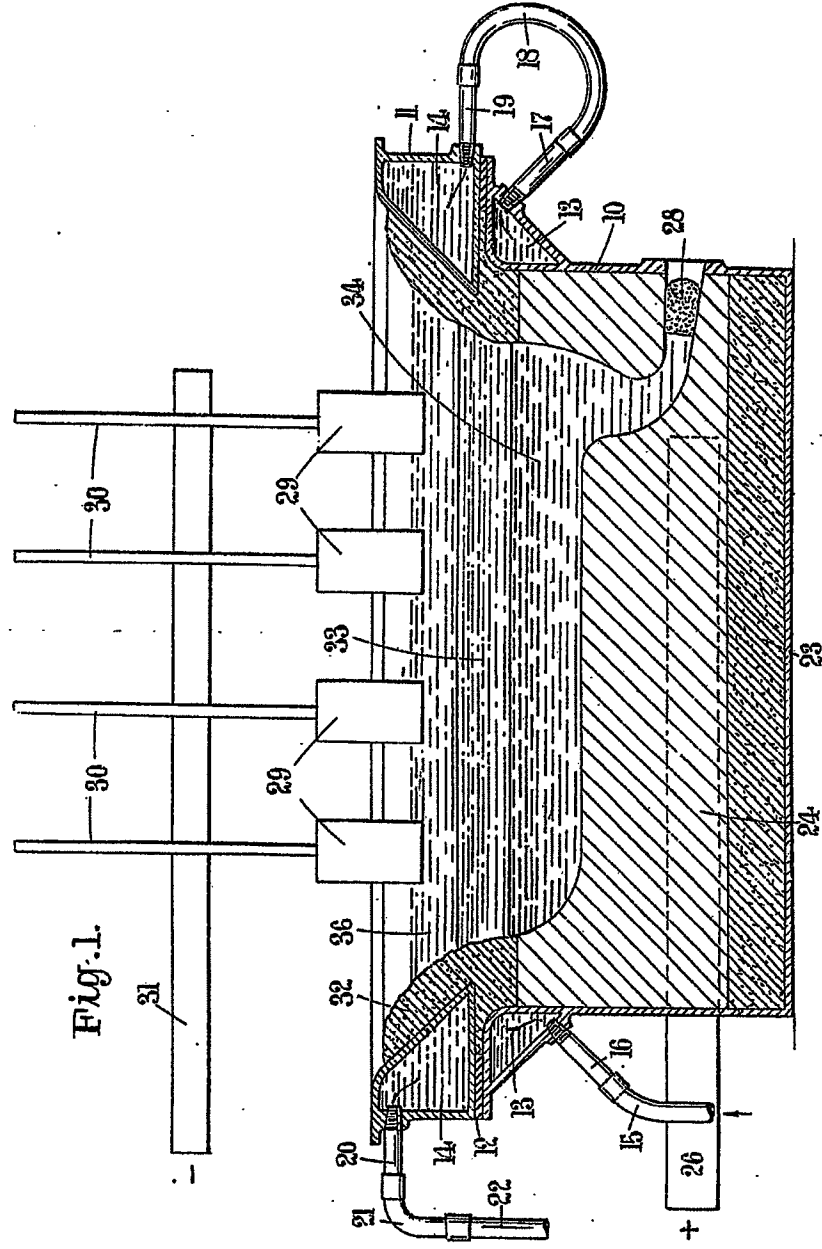
For
ALUMINUM COMPANY OF
AMERICA,

White, Langner, Stevens & Parry,
Chartered Patent Agents,
Jessel Chambers, 88—90, Chancery Lane,
London, W.C. 2, and
177, William Street, New York, U.S.A.



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